A VARNISHING COMPOSITION, A METHOD OF MANUFACTURING THE COMPOSITION, A COATED WINDING WIRE, AND A RESULTING COIL

The invention relates to filled hybrid varnishes, in particular for wires used in windings, and to winding wires covered in such varnish.

BACKGROUND OF THE INVENTION

Winding wires insulated by layers of varnish are used, for example, in the manufacture of coils for variable frequency controllers and converters.

In addition to their primary function of providing insulation, the varnishes used must also have sufficient ability to withstand high temperatures. Standard winding wires comprise a wire of conductive material, generally copper, covered in one or more layers of varnish of the polyester imide (PEI) type and/or of the polyamide imide (PAI) type in the highest temperature class, and they can withstand 200°C for 20,000 hours. Using polymide (PI) increases temperature class up to 250°C, but at the cost of lower ability to withstand partial discharges.

The appearance of more severe temperature constraints, particularly in applications for frequency converter motors, has nevertheless required varnish to be developed with better high temperature performance.

Thus, varnishes have recently been described comprising both organic portions and mineral portions in a single phase. Such varnishes are also known as "hybrid" varnishes. Such varnishes based on precursors for ceramics are described by K. Asano, K. Suzuki, S. Itonaga, and Y. Tetsu in Hitachi Cable Review, No. 16 (August 1997), 67-74. Because of the brittleness and the hardness of ceramics, the precursor such as a silicone or a polycarboxysilane is transformed into a ceramic only after the coil has been wound. After being subjected to special heat treatment, those varnishes withstand temperatures of up to 400°C. However, it would appear that that technique has not led to any application on an industrial scale.

Varnish for winding wires must also have considerable mechanical strength associated with adequate flexibility in order to ensure that the varnish does not crack, in particular while the wires are being wound into a coil.

Finally, new applications, e.g. in converters, also require the ability to withstand voltage peaks that are particularly high. Winding wires can be exposed to large transient peaks. Furthermore, these peaks can present fronts rising at speeds in excess of 1 kilovolt per microsecond (kV/μs). A winding wire can also be exposed to voltage peaks of this type while at high temperature, i.e. above 180°C. Stresses of this type can give rise to undesirable partial discharges. Such discharges give rise to electrical aging of the insulation by eroding the varnish coating. When in the presence of a gas such as air, a term used is "Corona aging".

In order to obtain insulation of winding wires that is durable, the varnish must thus withstand such transient voltage peaks in order to avoid damage to the motor and premature operating breakdowns.

Varnishes are known for winding wires that include special formulations for withstanding Corona type discharges. Document US–4 503 124 describes an example of a varnish composition comprising a polymer resin filled with alumina particles of a size smaller than 0.1 micrometers (μm). However, those varnishes present an unsatisfactory temperature rating.

Document US–5 654 095 describes a protective coating that can withstand voltage peaks approaching 3000 V, rise times of less than 100 kV/μs, and temperatures of up to 300°C. That protective coating comprises a resin and a filler in the form of particles of sub-micrometer size, such as particles of metal oxides, silica, and clays. Nevertheless, that protection necessarily requires a base insulation layer, thereby leading to a method that is complicated. In addition, the mechanical strength of

those varnishes is poor, particularly when wires coated in varnish are subjected to mechanical deformation prior to winding. That type of wire can then lose its ability to withstand Corona aging. It has been found that its lifetime can be reduced by 90% if the wire is subjected to prior stretching of 10%.

Document WO 98/25277 describes a hybrid varnish obtained by condensing silicon compounds, optionally together with other elements, in the presence of water. Adding fine particles of silanized glass as a filler is also mentioned. Those varnishes present poor ability to withstand partial electrical discharge at high frequency and they are unsatisfactory, even at low frequency, at temperatures in excess of 150°C.

Finally, document EP—0 768 680 describes a hybrid varnish to which particles of SiO_2 of a size lying in the range 50 nanometers (nm) to 100 nm can be added in order to increase the mineral content of the varnish. No mention is made of any effect due to the presence of such particles and concerning ability to withstand partial discharges or voltage peaks.

OBJECTS AND SUMMARY OF THE INVENTION

There therefore exists a need for winding wires having the above-mentioned properties, and in particular improved ability to withstand partial discharges and voltage peaks at high temperature.

The varnish of the invention makes it possible to mitigate the drawbacks of the prior art.

More particularly, the invention proposes a composition comprising:

a) a copolymer obtained from a thermoplastic or thermosetting resin and containing at least one alkoxysilane; and

b) a mineral filler selected from compounds of B, Al, Ti, Zn, Zr, Cr, Fe, and silicates, and mixtures thereof.

The invention thus proposes a varnish that is hybrid and composite and that enables winding wires to be manufactured that, unexpectedly, present ability to withstand partial discharges that is greatly increased compared with wires coated in prior art varnish, particularly at high temperatures.

On the basis of studies they have undertaken in this field, the inventors have found that certain mineral fillers perform a capacitive function because of their high dielectric constant, and thus moderate partial discharges which appear in the insulation under the effect of electromagnetic stresses. The purpose of the fillers in the varnish of the invention is thus not to provide mechanical reinforcement, but to spread out electrical charge uniformly. That is why fillers in vitreous form, having a small dielectric constant or having small specific surface area are unsuitable.

When electromagnetic stresses associated with the appearance of partial discharges are applied to a wire coated in a composition of the invention, the induced electric charge is not dissipated but is stored on the surfaces of the grains of the mineral filler. Such storage spreads out the potential uniformly through the filled hybrid layer of the invention and avoids the insulation being degraded and the dielectric breaking down, thereby increasing the lifetime of the insulation. The accumulation of electric charge and the relatively high dielectric dissipation values nevertheless imply that energy is accumulated in the material mainly in the form of heat, and they thus imply a thermal degradation mechanism.

However, this degradation mechanism can be slowed because of the higher temperature rating of a hybrid organic/mineral matrix.

Thus, combining two types of material makes it possible to increase significantly the lifetime of wires under high levels of stress (both thermal and

electromagnetic). Furthermore, even under stresses that are less severe, winding wires covered in this way present lifetimes that are subject to smaller standard deviation.

Advantageously, the thermoplastic or thermosetting resin is selected from the group comprising: polyamide imide (PAI), polyester imide (PEI), polyimide (PI), polyester (PE), polyurethane (PU), polyvinylacetal (PVA), and mixtures thereof.

In an advantageous embodiment, the copolymer is obtained by adding 10% to 50%, and preferably 20% to 40% by weight of alkoxysilane.

The alkoxysilane can be a tetraalkoxysilane such as tetraethoxysilane (TEOS), or a trialkoxysilane such as trimethoxysilane or aminopropyl-trimethoxysilane. Nevertheless, it is also possible to envisage other silicon compounds capable of copolymerizing with the polymer.

Ability to withstand partial discharges, voltage peaks, and Corona aging is considerably improved by adding mineral fillers selected from oxides or nitrides of B, Al, Ti, Zn, Zr, Cr, and Fe, and preferably titanium dioxide, and from silicates such as clays, in particular nanocomposite clays, mica, etc.

The mineral fillers are preferably added at a concentration of 2% to 20% by weight, with concentrations in the range 5% to 15% being particularly preferred.

It is assumed that the function performed by the mineral fillers is that of acting in a capacitive role due to their high dielectric constant. Furthermore, they enable electric charge to be stored.

In the composition of the invention, high specific surface area thus contributes to obtaining a considerable improvement in resistance to the Corona effect. Thus, mineral fillers presenting a specific surface area greater than 40 square meters per gram (m^2/g) are preferred.

In addition, high porosity is advantageous insofar as it enables electric charge to be trapped.

The rheological and other properties of the resulting varnish can be modified in the usual way.

The composition can be used as an insulating varnish for winding wires.

The invention also provides a method of manufacturing the above-defined composition, the method comprising the following steps:

· copolymerizing the thermoplastic or thermosetting resin with at least one alkoxysilane;

· adding a mineral filler selected from compounds of B, Al, Ti, Zn, Zr, Cr, Fe, silicates, and mixtures thereof; and

· homogenizing.

In most applications, it is desirable for the varnish to have low viscosity. Under such circumstances, it is advantageous to add a solvent. For polymers of the polyimide, polyester imide, and polyamide imide type, suitable solvents are ortho-cresyl, meta-cresyl, para-cresyl, cresylic acid, N-methylpyrrolidone, dimethylacetamide (DMAC), and mixtures thereof, and they are particularly advantageous.

The reaction between the organic portion, i.e. the polymer, and the mineral portion, i.e. the alkoxysilane, can be undertaken in the presence of a catalyst. This reaction is preferably performed with paratoluene sulfonic acid (pTSA), dibutyltin Bu_2SnO, or polysiloxanes. Such polysiloxanes include, for example, polydimethyl siloxane, silikophen ®, or silikophtal ® (both sold by TEGO).

The invention also provides a method of manufacturing such a winding wire, the method comprising the following steps:

· applying a varnish comprising the above-defined composition on the wire; and

· then setting the varnish.

The invention also provides the winding wire obtained by the manufacturing method, and a coil comprising such a conductor wire covered in such a varnish.

The resin is modified by adding inorganic compounds in conventional manner. Indications concerning suitable compounds and how to implement them can be found, for example, in patent WO 98/25277.

The conductor wire, made of a metal such as copper or aluminum, is coated in the varnish of the invention in conventional manner and is then dried. In particularly advantageous manner, the varnish can be applied directly on the wire. Nevertheless, it is also possible to apply the varnish to a wire that has already been provided with a layer of a composition serving to improve adhesion, for example. Such a coating can be performed, for example, using tris(2-hydroxyethyl) isocyanurate (THEIC). Thereafter, the varnish is set, preferably by heat treatment. Nevertheless, other treatments can be envisaged, for example using ultraviolet light. Similarly, the winding wire coated in the varnish of the invention can subsequently be covered in additional layers.

DETAILED DESCRIPTION OF THE INVENTION

The invention is explained in greater detail below by means of implementation examples given for illustrative and non-limiting purposes.

<u>EXAMPLE 1</u>

A polyesterimide (PEI) was prepared in cresylic solvents by reacting a diamine such as methylene dianiline (MDA) and trimetllitic anhydride (TMA) and a hydrolyzed aromatic polyester.

The polyesterimide was modified by adding 10% to 50% alkoxysilane such as tetraethoxysilane (TEOS), trimethoxysilane, or aminopropyl-trimethylsilane, optionally in the presence of a catalyst such as pTSA,

dibutyltin Bu_2SnO, or a polysiloxane such as polydimethyl siloxane, silikophen ®, or silikophtal ®.

Thereafter, 2% to 20% by weight (relative to the solids content of the solution) were added of a mineral filler such as TiO_2, Al_2O_3, ZnO_2, BN, clays, nanocomposite clays, and mica, and the solution was mixed until homogeneous.

EXAMPLE 2

A polyesterimide (PEI) was prepared in cresylic solvents by reacting a diisocyanate such as methylene diisocynate (MDI) with trimellitic anhydride (TMA) followed by esterification or transesterification in the presence of compounds possessing two or more hydroxyl bonds, such as tris(2-hydroxyethyl) isocyanurate (THEIC), dialcohols, glycols.

This polyesterimide was modified by adding 10% to 50% alkoxysilane such as tetraethoxysilane (TEOS), trimethoxysilane, or aminopropyl-trimethylsilane, optionally in the presence of a catalyst such as pTSA, dibutyltin Bu_2SnO, or a polysiloxane such as polydimethyl siloxane, silikophen ®, or silikophtal ®.

Thereafter, 2% to 20% by weight (relative to the solids content of the solution) were added of a mineral filler such as TiO_2, Al_2O_3, ZnO_2, BN, clays, nanocomposite clays, and mica, and the solution was mixed until homogeneous.

EXAMPLE 3

A polyamide imide (PAI) was prepared in solvents of the N-methylpyrrolidone (NMP) or dimethylacetamide (DMAC) type by reacting a diisocyanate such as methyldiisocynate (MDI) with trimetllitic anhydride (TMA).

The polyamide imide was modified by adding 10% to 50% alkoxysilane such as tetraethoxysilane (TEOS), trimethoxysilane, or aminopropyl-trimethylsilane, optionally in the presence of a catalyst such as pTSA,

dibutyltin Bu_2SnO, or a polysiloxane such as polydimethyl siloxane, silikophen ®, or silikophtal ®.

Thereafter, 2% to 20% by weight (relative to the solids content of the solution) were added of a mineral filler such as TiO_2, Al_2O_3, ZnO_2, BN, clays, nanocomposite clays, and mica, and the solution was mixed until homogeneous.

EXAMPLE 4

A polyimide of the Pyrel M® type (available from E.I. Dupont de Nemours & Co.) was modified by adding 10% to 50% alkoxysilane such as tetraethoxysilane (TEOS), trimethoxysilane, or aminopropyl-trimethylsilane, optionally in the presence of a catalyst such as pTSA, dibutyltin Bu_2SnO, or a polysiloxane such as polydimethyl siloxane, silikophen ®, or silikophtal ®.

Thereafter, 2% to 20% by weight (relative to the solids content of the solution) were added of a mineral filler such as TiO_2, Al_2O_3, ZnO_2, BN, clays, nanocomposite clays, and mica, and the solution was mixed until homogeneous.

The varnishes obtained in Examples 1 to 4 were applied to winding wires of diameter standardized by the IEC or the NEMA, using conventional techniques, e.g. by multiple coating or by spraying.

The thickness of the varnish layer was preferably of grade 1, 2, or 3 in the IEC 60 317—0—1 classification or in the class single, heavy, or triple in the NW 1000 classification from the NEMA.

The winding wires obtained in this way were tested under conditions simulating use in coils for variable frequency controllers and converters.

The results showed that the winding wires of the invention presented improved ability to withstand peak-to-peak voltages of up to 3 kV at a frequency of up to

20 kHz with rise times of up to 1 kV/μs at a temperature of up to 180°C.